Recent Technical Advances in Rice Bran Oil Processing (II About Refining Process)

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Synopsis: Recent advances in rice bran oil refining technology and its industrial status were reviewed. Partially, the history of producing technology of edible rice bran oil refining, and especially, the advance of physical refining of rice bran crude oil were discussed.

Several other items about this industry were also discussed.

1. Introduction

Rice bran oil technological research and its industry were first developed in Japan, where the staple food of people was rice, which was over-produced.

The authors have been engaging in this industry for more than fourty years. In these decades many reviews and abstracts were summarized by several researchers,[1-3] especially by the members of IUFST, S. Barber and B. Barber.[4] B. O. Juliano[5] has edited "Rice, Chemistry and Technology, 2nd ed." published as AACC Monograph Series (1985). He reviewed and abstracted most recent data in this field. Those new statistic data concerned up to 1985. However, one of the refered literatures, "Y. Takeshita,[6] Vegetable Oils and Fats. Manuf. Technol. Guide: No. 1" edited by Japan External Trade Org., Tokyo (1980)might be revised in the present status, because rice bran oil production increased in many regions, and the annual production of rice bran oil in the world has reached to about 450000 t.

For recent three years, Takeshita, one of the authors engaged in rice and rice bran oil industries developing project in Burma by OECF fund of Japanese government as a staff of consulting department of OMIC. And he was in charge of specification for rice bran stabilization. He stayed in Rangoon for one month, and also visited R. M. Sounders and R. N. Sayre,[7] in their laboratories at USDA, Western Region. Rese. Centre in Albani, California, and a demonstrating rice mill of extrusion cooking stabilizer. On the other hand, Sayre visited Japan recently to inspect and discuss rice bran oil industry. His research on stabilizing of an oil ingredient rice bran is an old but new theme in Asia. So, he and the authors discussed that theme with A. Noguchi, M. Yamasaki et al.[17] at National Food Research Institute of Tsukuba City.

Some other items which recently advanced in this field will be listed in the following paragraphs.

2. Recent advanced items in the rice bran oil industry

Recent technological and scientific advances in this industry are summarized in the following ten items.

1) Physical refining for edible purpose
2) Solvent refining and dewaxing

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3) Stabilizing of raw rice bran
4) Glycerin esterification of high acid value rice bran crude oil or distilled fatty acid from crude oil and acidulated soapstocks
   a) catalyst
   b) qualities of product
5) Ultra membrane filtration for refining
6) Fine chemicals separations
   a) Oryzanol (ferulic acid ester of triterpene alcohol)
   b) Inositol from defatted bran
   c) Tocopherols (d-α-tocopherol)
7) Selection of processing
   a) Solvent extraction
   b) Hydraulic press and screw press in a small industry
8) Speciality of rice bran oil components
   a) Linolenic, arachidic and gadoleic acids isolation
   b) Phenolic substance
9) Energy conservation in processing
10) Waste problem

These items, except the last two, are detailed in Discussions.

3. Discussions

Rice bran is a fine grain byproduct of milling and polishing. Its oil is stable and premier edible after refining, and its byproduced distlled fatty acid is a superior material of synthetic resin. The ratio of edible oil to industrial oil is 7:3 for crude oil statistically in Japan, where the average acid value of crude oil is 23–25.

The present ordinary rice bran oil mills are continuous type, which have the capacity of 50–200 t/d, and those in smaller plants are generally batch type, which have the capacity less than 30 t/d, recently observed in the s. e. Asia. The percolation system extractors are distributed in the continuous plants rather than those of immersion system.

The mechanical press or screw press is used locally, and is suitable to the small capacity oil mill attached to a rice mill for treating fresh raw rice bran. In such case, average acid value of extracted crude oil is less than 10, however, oil yield from bran containing 15–20% oil ranges 10–18%.

Recently the stabilization of raw rice bran by extrusion cooking without deterioration of oil component, solvent refining or physical refining and solvent dewaxing were improved again.

As the results, the production cost and the quality of edible oil were improved, and pharmaceutical byproducts, for examples oryzanol and inositol were developed. The polution problems of liquid waste were also minimized. Of course, energy conservation was considerably accompolished. Now the items described in paragraph 2 are discussed as follows.

1) Physical refining for edible purpose

The physical refining of rice bran oil was researched by Hitotsumatsu et al.[14] of Tokyo Oil and Fat Co., who were the pioneers of rice bran oil edible refining, before the 2nd World War. However, after the war S. Nakazima et al.[15] first succeeded in the physical refining which was industrialized by Tokyo Oil & Fat Co., Ltd. and Nitto Chemical Co., Ltd. That physical refining project was closed after about ten years from the opening due to the influence of market.

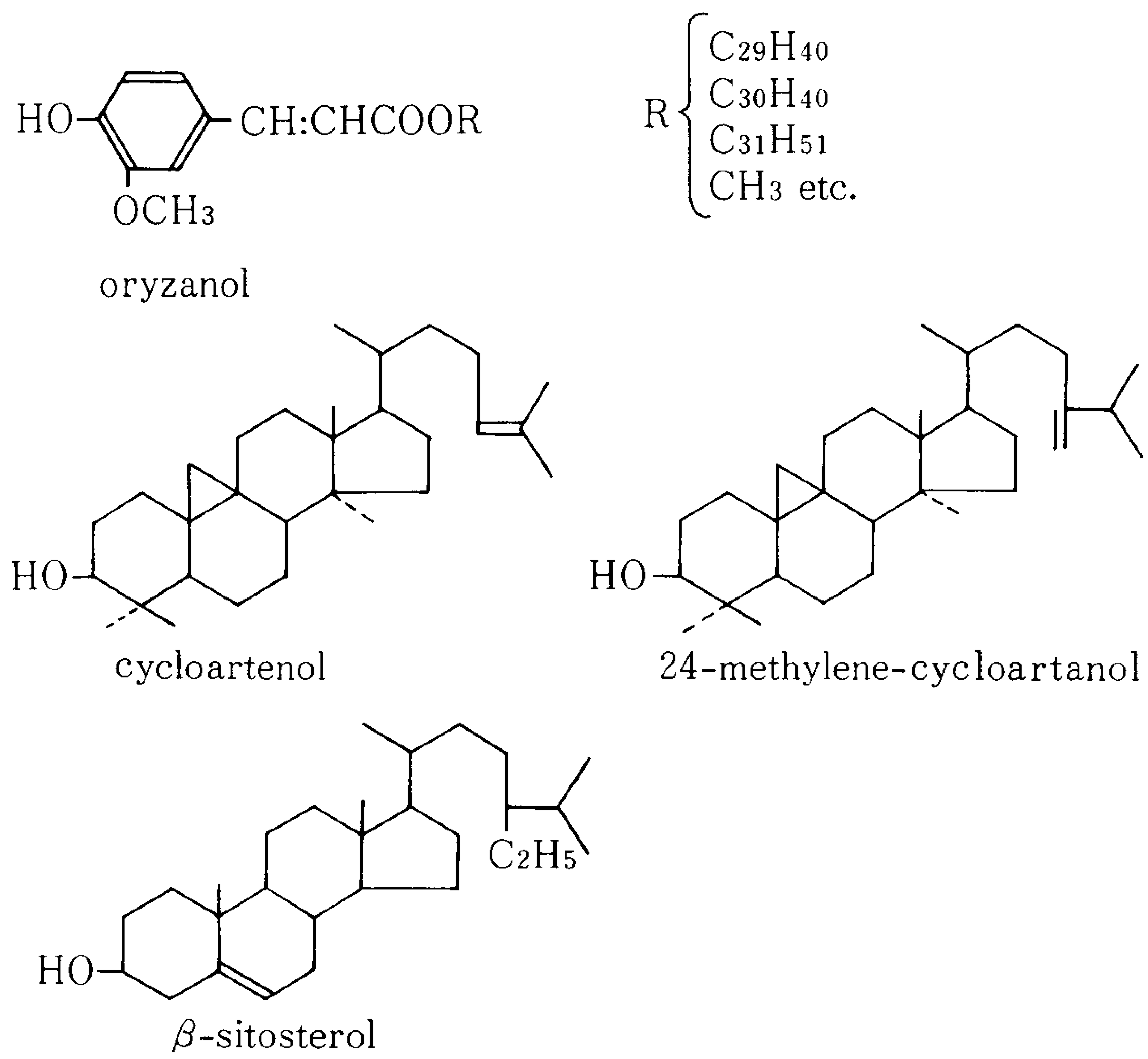
The authors had developed a physical refining of other several kinds of vegetable oils and patented, furthermore, a lot of plant makers offered such facility. About palm oil, 400 or 200 m/t/d capacity plants are now in operating. But the alkali refined palm oil has some superior qualities than the physically refined oil.

On the other hand, in rice bran oil refining, it was diffucult to get a good result, because rice bran crude oil required the special technique for refining. In Japan, the physical refining plant of rice bran oil is operating only in two factories. In spite of palm oil refining plant's 2–4 Torr vacuum and several ten min retention, the new rice bran oil refining plant is developed to one order low conditions by Nihon Vacuum Technological Co., Ltd., and its plant capacity is 50–100 m/t/24 h. The yield of refined oil is nearly equal to the case of solvent refined oil, and the energy conservation and polution problem are solved considerably. However, it needs to prepare the crude oil, and phenolic substance can not be removed by the vacuum distillation, and the substance must be removed by the following alkali refining **(Figs. 1 and 2).**

2) Solvent refining and dewaxing

Solvent refining of high acid value oil and solvent dewaxing were first developed for cotton seed oil refining. But rice bran oil, corn oil and olive oil are comparatively high acid value crude oils, therefore, the solvent refining is effective for these crude oils.

There are two kinds of solvent refining process. The one is DeLaval and the other is binominal NEUMI. The latter has better yield of refined oil but spent more thermal energy. Economically, there is a tendency to avoid the solvent refining and to use ordinary alkali



dihydro-β-sitosterol ferulic ester $C_{39}H_{60}O_4$
dihydro-γ-sitosterol ferulic ester $C_{39}H_{60}O_4$
eicosanol 〃 $C_{30}H_{50}O_4$

Fig. 1 Oryzanols & Triterpenoids. (by A. Kato[12])

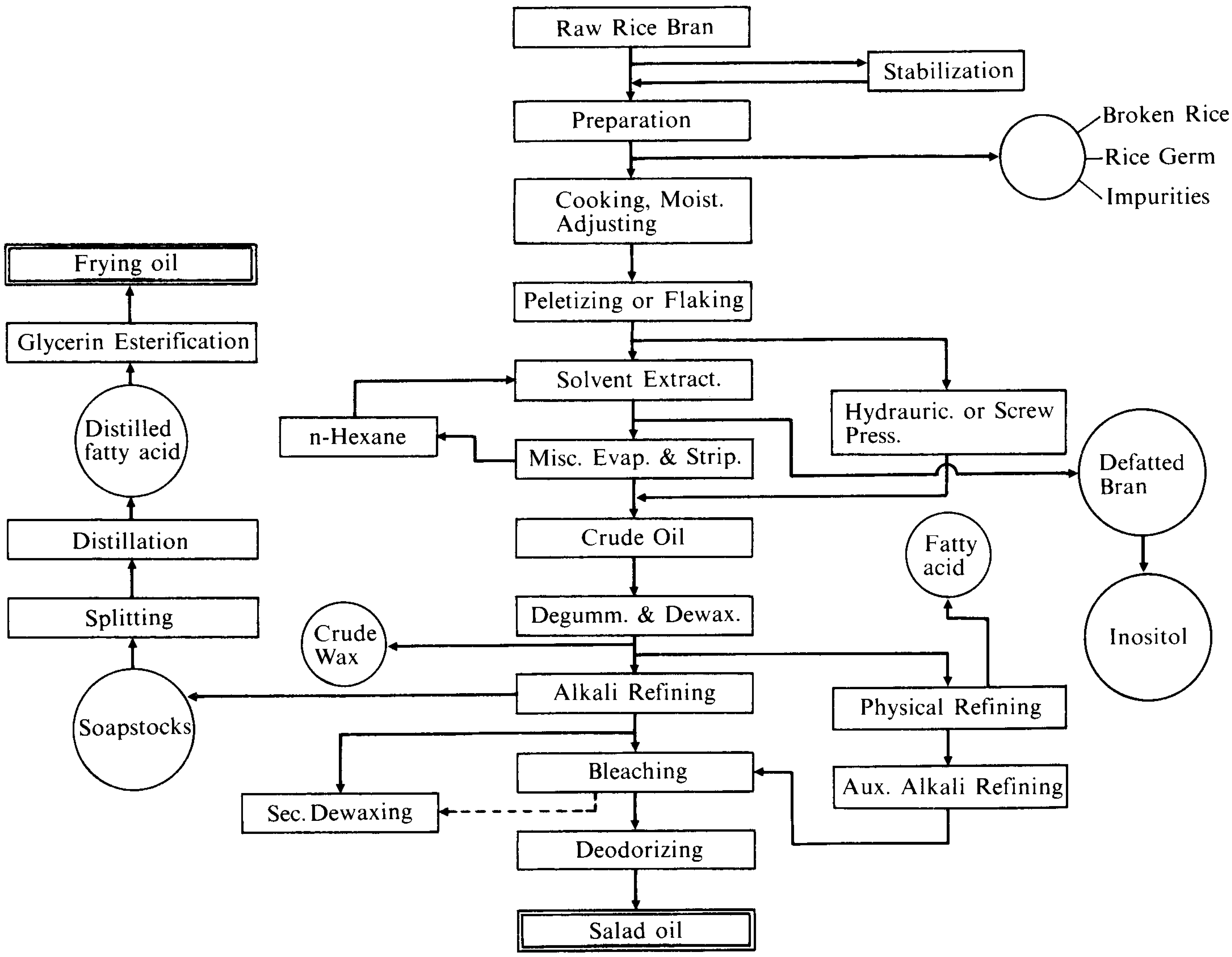


Fig. 2 Flow Sheet of Rice Bran Oil Processing.

refining process for saving steam. However, the refining loss in the binominal solvent refining is about 60% of ordinary alkali refining process. Not isopropanol (*sec*-alcohol) but ethanol (primary alcohol, easy esterifying) is a hygienically registered solvent in Japan. Even in the solvent dewaxing, the first step of it is alternated by nonsolvent process with high efficiency automatic filter. n-Hexane or acetone is a hygienically registered solvent. Rice bran wax yield from crude oil by solvent fractionation is about 3%. Higher aliphatic alcohol isolation was developed recently, and hydrogenated waxy oil was also produced, but the other part of waxy oil has not fully essential use. The potential production of rice bran wax is more than the quantity of carnauba wax in the south America.

3) Stabilizing of raw rice bran

Rice bran lipid hydrolyses rapidly by an enzyme, so called lypase produced by some microbe, which can be inactivated by high temperature keeping or chemicals. These processes were researched in Japan for half century.

But at the present status, the stabilization process was not utilized in Japan, because rapid collection of rice bran from rice mill had been achieved, and the capacity of oil mill was excess to ingredient bran supply.

In the ordinary case like in Burma, the condition is different, and the stabilizing is very useful, because the location of rice mill and rice bran oil one are dotted and the traffic condition is not suitable to rapid collection of bran. In these status, the stabilization by extrusion cooking researched by USDA is important.

Heat stabilization needs simple equipments, with or without steam, electricity or fuels (rice hull is available to generate steam). However, the oil component of treated bran deteriorates, and bleaching process is difficult. However, the merits are low running cost and long life of equipment. In China Republic or Burma, some rice mills are using this process. But extracted rice bran oil is difficult for edible refining, and treated bran gets frequently red burned color. The storage period under ordinary package is short. If the steam is used to avoid air, such deterioration will not be seen. On the other hand, the treated bran by extrusion cooking method showed good quality, and it needed no pelletizing process as the preparation to solvent extraction. But the demerits are necessity of large capacity of electric power and wear of mechanical parts.

According to Sayre,[7] the power consumption is only 0.076 kwh/kg, at 130°C, for 10-15 sec. and 98°C, for 3 min, in spite of need of large electric motor.

In the case in USA or Japan, where electricity supply is easy, this process is suitable, however in developing countries, where electricity supply is difficult or unit price of electricity is expensive, domestic power station or fuel engine must be provided. Recently, the Brady type and Instapro type are put on the market. The authors recommended the extrusion cooking stabilizing for Burmese rice bran oil project, and permitted heat stabilization as the only alternative process in the case that electricity suply was poor.

Abhay Sah et al.[8] reported that influence of pellet size on extraction rate of rice bran oil was negative.

However, C. J. Kim et al.[9] compared solvent extraction characteristics of rice bran pretreated by hot air drying, steam cooling and extrusion. As the result, pelletized or extruded rice bran showed largest extraction rate to other pretreated brans. According to the authors' consideration, even if extrusion cooking needs excess energy and equipments, practically no pelletizing machine for pretreating to solvent extraction is necessary. A flaking or pelletizing for solvent extraction by high power electric motor will be eliminated by the extruding stabilization.

Items 4)–8)

There are two types of reesterification of rice bran oil. The one is deacidification of high FFA crude oil by reesterification and alkali neutralization, reported by A. C. Bhattacharyya[10] and D. K. Bhattacharyya [11] of India.

It was a historical method in Japan. This method has two points for discussion i.e. quality for edible purpose and hygienic prohibited catalyst.

Until recent years, colored oil by this method was seen in the south east Asia, with a

Table 1 Recently Investigated Acid Values of Industrial Oils[3]

Sample	AV \ Indicator	PP	AB	Diff
crude or refined rice bran oil	mainly solvent-refined oil	0.08	0.02	0.06
		0.09	0.03	0.06
		0.10	0.05	0.05
		0.12	0.03	0.09
	general refined oil	0.18	0.03	0.15
		0.28	0.03	0.22
	crude oil	37	35	2

Sample	AV \ Indicator	PP	AB	Diff
corn germ oil	crude oil	6.35	6.29	0.06
		3.18	3.12	0.06
	refined oil	0.07	0.05	0.02
		0.08	0.05	0.03
		0.12	0.10	0.02
wheat germ refined oil		0.19	0.15	0.04
rape seed oil	crude	1.37	1.37	0.00
	refined	0.03	0.03	0.00

hygienic problem, but lately it is rare in the market.

The other is to esterify the distilled fatty acid from splitting of crude oil or soapstocks. This process is the same one to MCG synthesizing which is popular in the world. Formerly, K. Sakurai[13] molecular-distilled low grade synthetic triglyceride, and manufactured good quality salad oil. However, it did not show good paying in the market application.

Ultra membrane filtration for refining is industrialized step by step, in degumming, dewaxing and partial bleaching pretreatment.

Fine chemicals isolating as the byproducts of rice bran oil industry is already popular. Recently, some patents were opened, finishing effective period, though the manufacturing technology includes much knowhow, and market demand is not so big. Rice bran fine chemicals production was industrialized in Korea or Republic of China also.

Natural tocopherol in rice bran oil has more rich content of d-α- tocopherol than those in other vegetable oils, and rice germ oil contains more quantity of tocopherol than bran oil.

In a small factory, small capacity oil extractor is better than large one. Mechanical extractor or small screw press has yet industrial life at local mills.

In Japan, 30 t/day batch extractor is used. In China Republic there are still many hydraulic presses and some small capacity screw ones even in cities. They are locally effective and reasonable.

About speciality of rice bran oil component, A. Kato[16] and the authors developed a method to isolate linolenic acid, arachidic and gadoleic acids of rice bran oil, independently, by GLC with EGS and EGA column.

From these results, oxydation stability of rice bran edible oil depends on minor content of linolenic acid also. The remained peak area of GLC pattern in which DEGS column corresponded to errored linolenic acid was confirmed as arachidic and gadoleic acids. The authors checked this composition by separating C-18 and C-20 acids through perfect hydrogenating of whole rice bran fatty acid methyl ester. The authors recommend EGA or EGS column for analysing the fatty acid composition of C-20, F=0 & 1 with C-18, F=3 acid, without using DEGS column. S. Yamasaki[17] reported another isolating method of C-20 acids.

Phenolic substance is universal in cereal lipids, and crude rice bran oil contains about 2% as oryzanol. Even in refined rice bran oil, a part of oryzanol remains, and influences to acid value obtained with phenolphthalein indicator. (**Table 1**).

Japan Agric. Standard established Alkali Blue-6B or Brom-Thymol-Blue as the indicator for AV titration of rice bran and corn oils, by one of the authors' advice.[3]

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米ヌカ油工業技術の最近の進歩

(II 精製法)

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要旨 米ヌカ油工業技術の最近の進歩について総説した。一部では食用米ヌカ油の技術開発の歴史について，特に『物理的精製法』については著者が研究と生産に関係してその実地について討論した。その他の新しい項目についても各論として述べた。

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